

Crystal Structure of Novel LTCC Microwave Ceramics

The progress of wireless communication devices largely depends on the development of microwave resonator ceramics with improved dielectric properties and reduced cost. Microwave ceramics with low sintering temperatures become of increasing importance as they (i) can be processed at significantly reduced cost for bulk applications and (ii) can be integrated in multilayer structures co-fired with metal electrodes. Detailed knowledge of phase equilibria and crystal-chemistry in such systems is imperative for the rational optimization of both processing parameters and dielectric properties. The present work demonstrates application of high-resolution transmission electron microscopy and X-ray diffraction to the analysis of crystal structures and phase equilibria of a novel low-sintering-temperature microwave ceramic in the Li-Ti-Nb-O system.

The solid solution $\text{Li}_{1+x-y}\text{Nb}_{1-x-3y}\text{Ti}_{x+4y}\text{O}_3$, also referred to as the “M-phase”, occurs over an extended phase field in the Li_2O - TiO_2 - Nb_2O_5 system. Recent work at the University of Pennsylvania has demonstrated that these solid solutions exhibit a combination of low sintering temperatures (1100 °C) and chemically tunable dielectric properties of interest for use in wireless communication systems ($\epsilon=55\text{--}78$, t_f tunable to zero, Q_f up to 9000 GHz). Moreover, the sintering temperature of these ceramics can be reduced to 950 °C by small additions of V_2O_5 , which permits co-firing with silver electrodes, thus rendering the ceramic an attractive candidate for LTCC technology.

Despite the technological potential of the $\text{Li}_{1+x-y}\text{Nb}_{1-x-3y}\text{Ti}_{x+4y}\text{O}_3$ solid solutions, their crystal-chemistry and exact chemical compositions have remained uncertain, rendering it difficult to understand and control dielectric properties. Two different models have been proposed to describe the crystal structure of the M-phase. According to one model, the structure is incommensurate and consists of intergrowths of LiNbO_3 -type and Li_2TiO_3 -type (rock-salt) blocks; the model implies stacking faults in the oxygen subcell. Another model suggested that the structure is an intergrowth of LiNbO_3 and $\text{Li}_4\text{Ti}_5\text{O}_{12}$ (spinel) blocks. However, no clear evidence was established to support either of these models.

In the present work, we applied electron diffraction and structural imaging in a high-resolution transmission electron microscope to clarify the crystal structure of the $\text{Li}_{1+x-y}\text{Nb}_{1-x-3y}\text{Ti}_{x+4y}\text{O}_3$ phase. Systematic studies confirmed that what actually forms is not a solid solution, but rather a homologous series of distinct compounds (Fig. 1) with structures built from LiNbO_3 -like blocks. Successive compounds differ in the thickness of the LiNbO_3 blocks, expressed as the number of cation (or anion) layers, n , which increases with decreasing Ti/(Li+Nb) ratio. The total number of layers in the repeat unit is $L=n+1$. The structure of LiNbO_3 features a hexagonal close-packed oxygen subcell with the interstices filled by Li and Nb cations; the cation layers in turn form a cubic close-packed stacking sequence. Computer simulations of the phase contrast for LiNbO_3 indicated that the stacking sequences of the anion- and cation-layers can be revealed using the [210] and [110] structural projections, respectively (Fig. 2). Application of this imaging code to the interpretation of the structural images of $\text{Li}_{1+x-y}\text{Nb}_{1-x-3y}\text{Ti}_{x+4y}\text{O}_3$ specimens demonstrated that both previous models were incorrect: The “M-phase” compounds feature intergrowths of LiNbO_3 -type blocks and corundum-like layers (Fig. 3), similar to the recently reported Nb_2O_5 -stabilized $\text{Li}_{14}\text{Ti}_{19}\text{O}_{45}$ phase. The stacking sequence of the oxygen ions

remains hexagonal close-packed for all homologs.

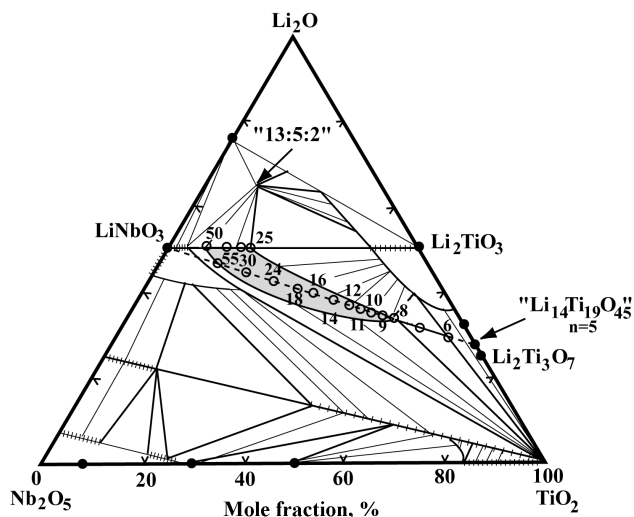


Figure 1: System Li_2O - Nb_2O_5 - TiO_2 at 1100 °C (Phase Equilibria Diagrams, Vol. XI, Fig. 9451). The “single-phase” field containing $\text{Li}_{1+x-y}\text{Nb}_{1-x-3y}\text{Ti}_{x+4y}\text{O}_3$ (M-phase) is indicated by gray shading. In the present study, rather than a continuous solid solution, a homologous series of distinct compounds (indicated by empty circles) were found to occur in this phase field. The numbers correspond to the number of cation layers, L , in the repeat unit.

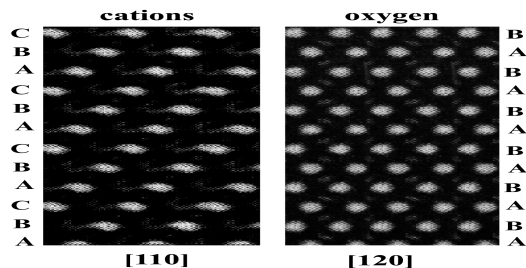


Figure 2: Computer simulated phase contrast images of LiNbO_3 in both the [110] and [120] orientations. These two projections reveal the stacking sequences of the cation and oxygen layers, respectively, and for the $\text{Li}_{1+x-y}\text{Nb}_{1-x-3y}\text{Ti}_{x+4y}\text{O}_3$ specimens, revealed that it is not a continuous solid solution, but rather a homologous series of distinct phases.

(Fig. 4). The M-phase field was confirmed to encompass a series of such ordered commensurate intergrowths with n ranging from 5 to 54. Specimens with compositions corresponding to fractional n -values typically contained a mixture of two compounds having the nearest integer n -values. Similarly, specimens with nominal compositions corresponding to large values of n contained a mixture of structures with a range of n -values close to the nominal value. For example, a specimen with a nominal composition corresponding to $n=27$ contained a mixture of structures with $n=24, 25, 26, 27, 28$.

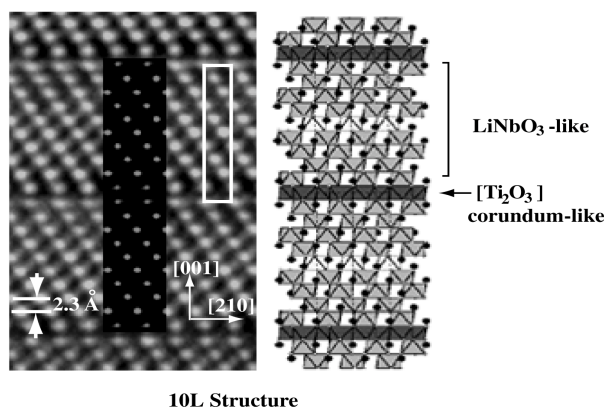


Figure 3: Structural image of the compound $\text{Li}_{9.5}\text{Nb}_{4.4}\text{Ti}_{7.1}\text{O}_{30}$ in the [110] orientation recorded near Scherzer defocus. The composition corresponds to a structure with $n=9$ (10 layers in the repeat unit). The insert shows the phase contrast calculated using the structural model shown, which features intergrowth of LiNbO_3 - and corundum-like layers. The model was derived by structural refinements using single-crystal X-ray diffraction data.

For a few compositions corresponding to small n -values, single crystals could be grown using a flux method and the structures of these crystals were solved using X-ray diffraction, in collaboration with Dr. I.E. Grey (CSIRO Minerals, Australia). The resulting structural models were in agreement with those proposed from electron microscopy data (Fig. 3).

X-ray structural refinements provided information about the distribution of Ti and Nb in the structure which could not be obtained using electron microscopy data. In particular, the refinements indicated that Ti preferentially segregates into the corundum layers, which, thus, have a composition of $[\text{Ti}_2\text{O}_3]^{2+}$.

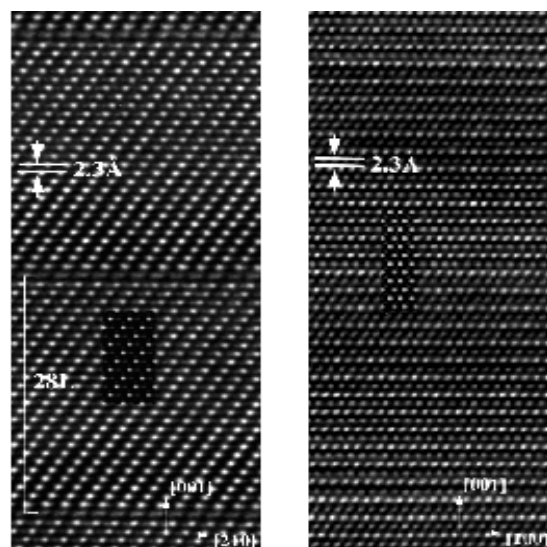


Figure 4: Structural images of the $\text{Li}_{1+x-y}\text{Nb}_{1-x-3y}\text{Ti}_{1+x+4y}\text{O}_3$ 28L-structure ($n=27$) in both [110] (left) and [120] (right) orientations. This compound is located on the LiNbO_3 - Li_2TiO_3 join. The [110] projection reveals cubic closed packed stacking of the cation layers in the LiNbO_3 -like blocks; the intergrowth of these blocks with the corundum-like layers is observed. The [120] projection demonstrates that the oxygen layers form a hexagonal close-packed stacking sequence which is continuous across the intergrowths. The contrast calculated for the LiNbO_3 structure is superimposed.

The symmetries of the $\text{Li}_{1+x-y}\text{Nb}_{1-x-3y}\text{Ti}_{1+x+4y}\text{O}_3$ compounds were derived theoretically for different n -values. The analysis demonstrated that all possible structures are represented by four distinct trigonal space groups; both the space group and the lattice parameter along the stacking direction are determined by the n -value. All four deduced space groups contain an inversion center (introduced by stacking of the LiNbO_3 -like layers), so that all $\text{Li}_{1+x-y}\text{Nb}_{1-x-3y}\text{Ti}_{1+x+4y}\text{O}_3$ compounds are predicted to exhibit paraelectricity, in contrast to LiNbO_3 . The predictions were in excellent agreement with experimental data.

The structural nature of the M-phase ceramics as complex mixtures of distinct compounds rather than a continuous solid solution bears important implications for their processing and properties as LTCC ceramics: The structural complexity and large number of possible phases considerably extends the “tunability” of properties in the $\text{Li}_{1+x-y}\text{Nb}_{1-x-3y}\text{Ti}_{1+x+4y}\text{O}_3$ system. However, processing temperatures and times will need to be carefully controlled in order to yield consistent phase assemblages and dielectric properties.

For More Information On This Topic:

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